# "Drop-in" Jet and Diesel Fuels from Renewable Oils

**11 May 2011**

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ReDi-Jet™

ReDi-Diesel™

APPLIED RESEARCH ASSOCIATES, INC.®

An Employee Owned Company

# Report Documentation Page

*Form Approved*
*OMB No. 0704-0188*



| 1. REPORT DATE | 2. REPORT TYPE | 3. DATES COVERED |
|---|---|---|
| **11 MAY 2011** | | **00-00-2011 to 00-00-2011** |

| 4. TITLE AND SUBTITLE | 5a. CONTRACT NUMBER |
|---|---|
| **'Drop-in' Jet and Diesel Fuels from Renewable Oils** | 5b. GRANT NUMBER |
| | 5c. PROGRAM ELEMENT NUMBER |
| 6. AUTHOR(S) | 5d. PROJECT NUMBER |
| | 5e. TASK NUMBER |
| | 5f. WORK UNIT NUMBER |
| 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Applied Research Associates Inc,4300 San Mateo Blvd. NE, Suite A-220,Albuquerque,NM,87110** | 8. PERFORMING ORGANIZATION REPORT NUMBER |
| 9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) | 10. SPONSOR/MONITOR'S ACRONYM(S) |
| | 11. SPONSOR/MONITOR'S REPORT NUMBER(S) |

12. DISTRIBUTION/AVAILABILITY STATEMENT
**Approved for public release; distribution unlimited**

13. SUPPLEMENTARY NOTES
**Presented at the NDIA Environment, Energy Security & Sustainability (E2S2) Symposium & Exhibition held 9-12 May 2011 in New Orleans, LA. U.S. Government or Federal Rights License**

14. ABSTRACT

15. SUBJECT TERMS

| 16. SECURITY CLASSIFICATION OF: | | | 17. LIMITATION OF ABSTRACT | 18. NUMBER OF PAGES | 19a. NAME OF RESPONSIBLE PERSON |
|---|---|---|---|---|---|
| a. REPORT **unclassified** | b. ABSTRACT **unclassified** | c. THIS PAGE **unclassified** | **Same as Report (SAR)** | **31** | |

# Overview

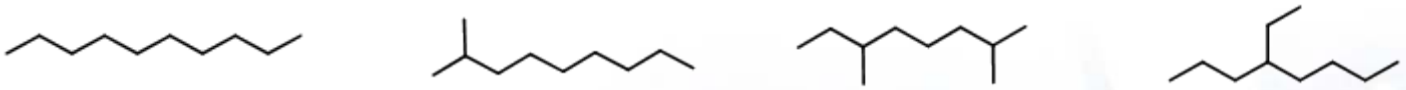
- ARA Introduction
- Catalytic Hydrothermolysis (CH) Process
- CH Product Chemistry
- Naphtha Data
- Recent Algal Oil Tests
- Byproduct Potential
- Pilot System
- Engineering Challenges
- Feed Stock Availability
- Commercialization Approach

# Current Alternate Fuel Technologies

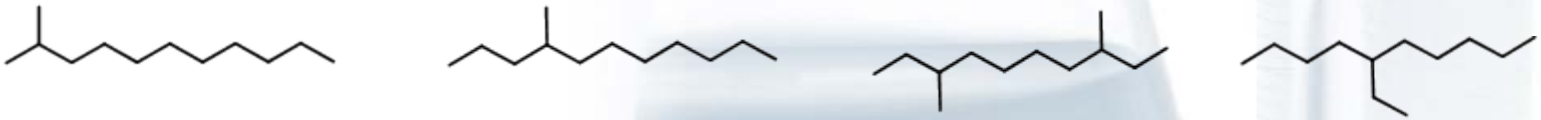
- **Fischer-Tropsch (FT) and Syngas Fuels**
  - First used in WWII Germany
  - Gasify coal or other biomass to CO and $H_2$
  - Catalytically convert syngas to hydrocarbons
    - Paraffins and isoparaffins
- **Hydrotreated Renewable Jet (HRJ)**
  - Converts renewable plant oils or fats
  - Conventional catalytic petroleum refining processes
    - Hydrotreating, hydrocracking, hydroisomerization
    - Produces paraffins and iso paraffins
- **Jet Fuel from Current Technologies Require Blending**
  - Up to 50:50 with petroleum-derived jet fuel
  - Alternate fuels exhibit low density – below specification requirement
  - Alternate fuels contain no aromatic compounds
    - Necessary for O-ring swelling

# Current Alternate Fuel Technologies

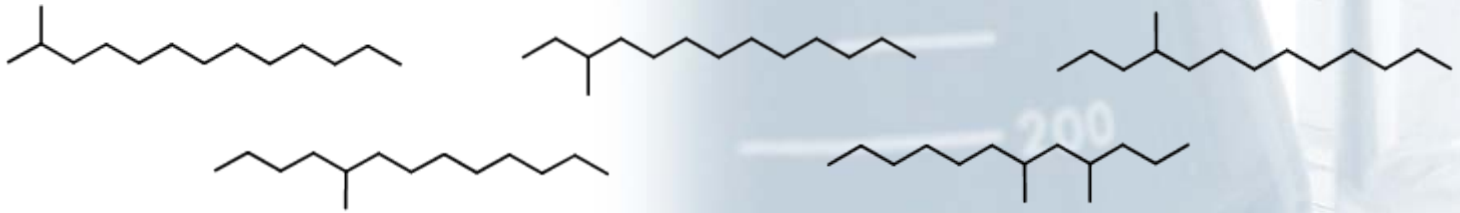
- **Typical jet fuel hydrocarbons from HRJ and FT**
  - **8 to 14 carbon paraffins are typical for the jet fuel fraction**
  - **C10 examples**



  - **C12 examples**



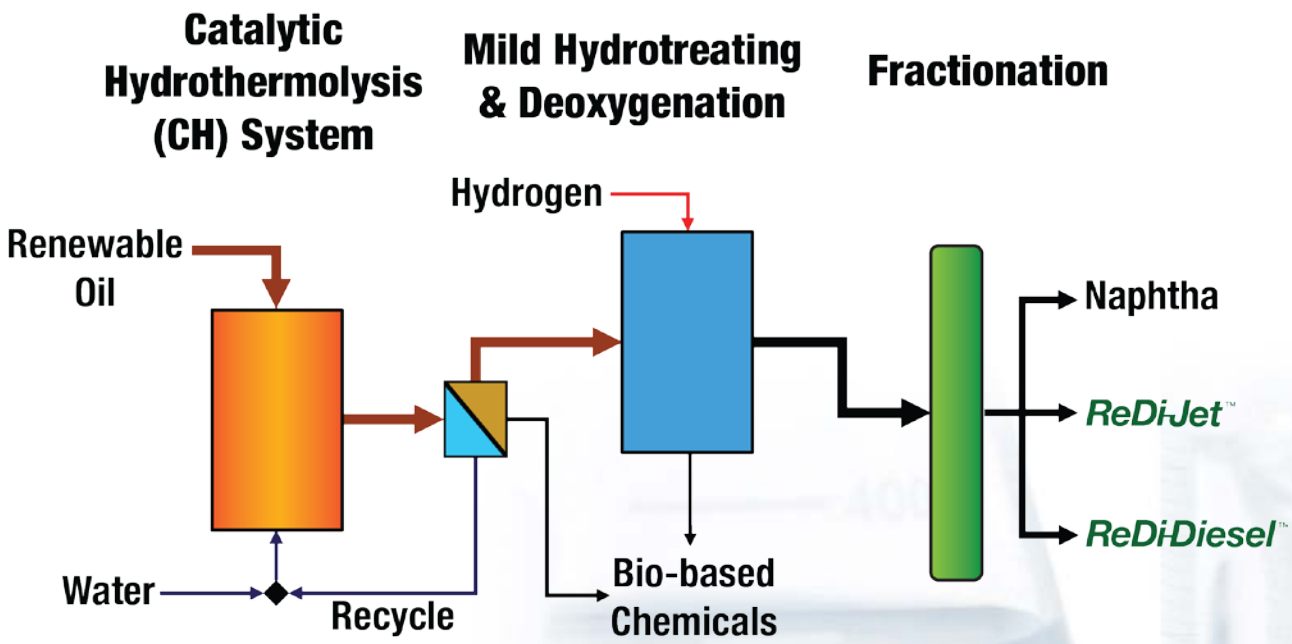
  - **C14 examples**



# CH Process Background

- ARA developed "Catalytic Hydrothermolysis " (CH) in 2006
  - A hydrothermal process where water mediates the CH reactions
  - Dr Lixiong Li, inventor, expert in hydrothermal technology
  - U.S. patent 7,691,159 was awarded April 6, 2010
- Goals of the CH process:
  - Produce ***Re***newable ***D***rop-***i***n Jet fuel – ***ReDi*** Jet™ and
  - ***Re***newable ***D***rop-***i***n diesel fuel – ***ReDi*** Diesel™
  - Avoid blending and equipment or infrastructure modifications
- A commercially viable process without subsidies
  - Reduce hydrogen consumption and carbon footprint
  - Eliminate hydrocracking, hydroisomerization and catalysts consumption
  - Produce valuable chemical byproducts
- Improve energy security

# ARA Hydrothermal Process *(patented)*

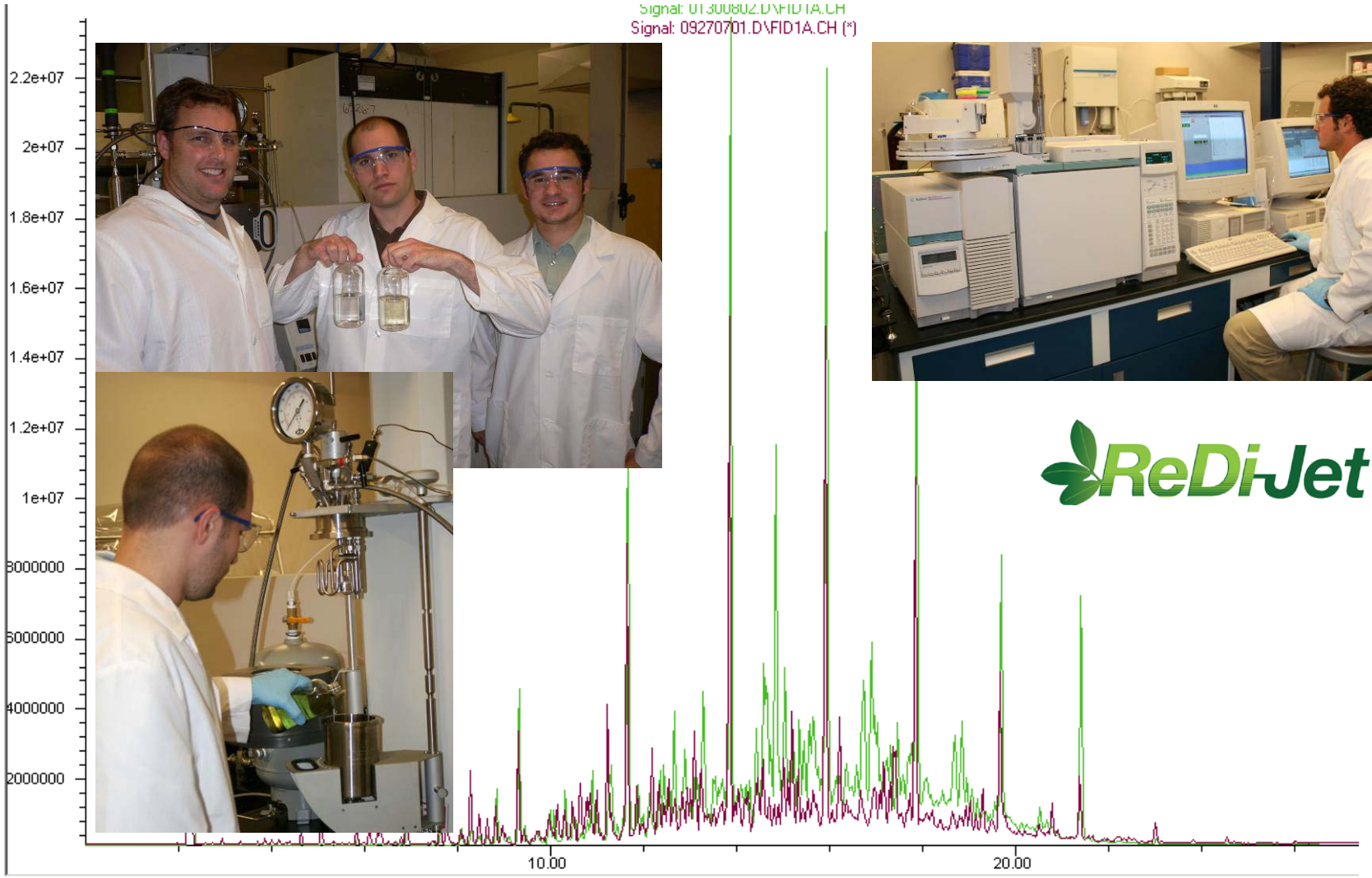



- Hydrolysis and cyclization reactions reduce hydrogen requirements compared to conventional hydrocracking and hydroisomerization
  - Reduces hydrogen consumption up to 74%
  - Reduces $CO_2$ generation up to 65%
- High-density cycloparaffins and aromatics are produced
- Valuable bio-based chemicals are produced

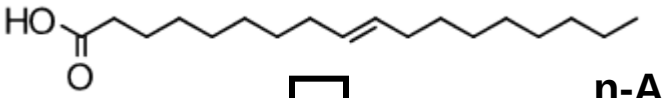
# Catalytic Hydrothermolysis Reactions

- Hydrolysis
- Isomerization of the double bonds in unsaturated fatty acids
- Decarboxylation of fatty acids to the corresponding paraffin
- Cyclization of unsaturated fatty acids into alkyl cycloparaffins and aromatics
- Cyclization of polyunsaturated fatty acids into alkyl aromatics
- Cracking of fatty acids into linear carboxylic acids and corresponding cycloparaffin
- Cracking of fatty acids into linear carboxylic acids and corresponding aromatics
- Formation of dicarboxylic acids
- Skeletal isomerization of intermediate and product compounds

# GC of ReDi Jet from CH and Petroleum JP-8



# Oleic Acid – Hydrothermolysis Products



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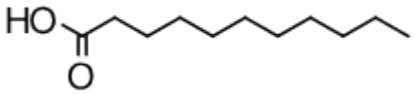
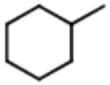
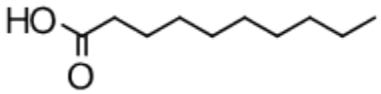
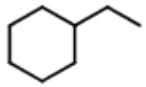
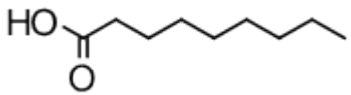
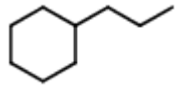
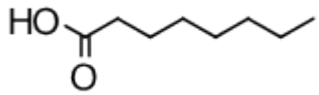
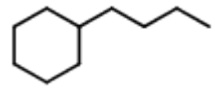
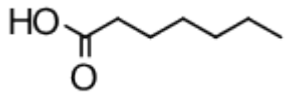
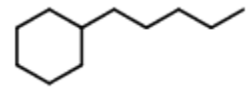
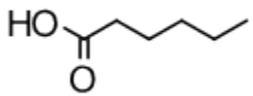
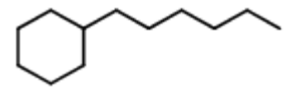
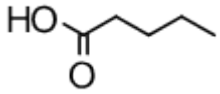
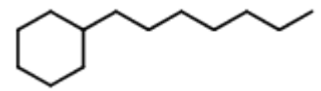
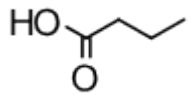
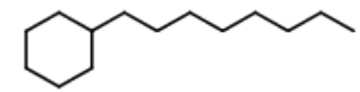
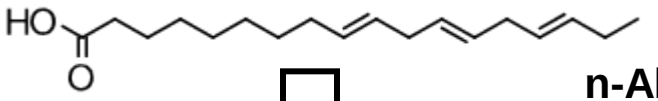
| C-11 |  | + |  C-7 |
| C-10 |  | + |  C-8 |
| C-9 |  | + |  C-9 |
| C-8 |  | + |  C-10 |
| C-7 |  | + |  C-11 |
| C-6 |  | + |  C-12 |
| C-5 |  | + |  C-13 |
| C-4 |  | + |  C-14 |

# Linolenic Acid – Hydrothermolysis Products



| Carboxylic Acids | | | n-Alkylbenzenes |
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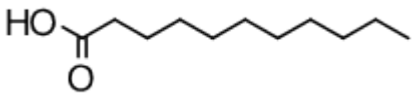
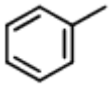
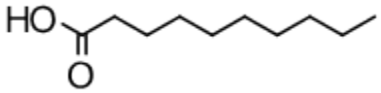
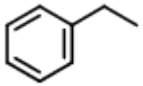
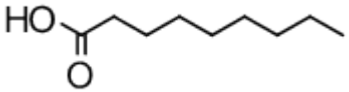
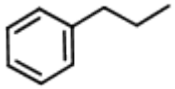
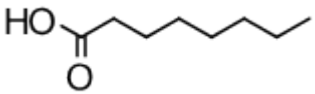
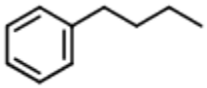
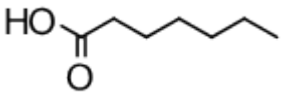
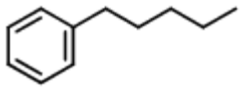
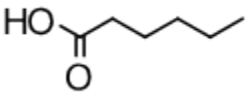
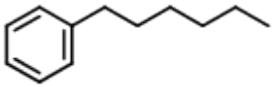
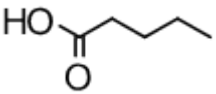
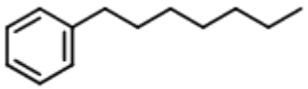
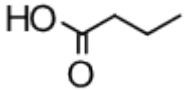
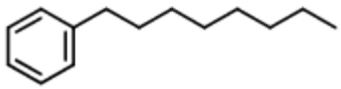
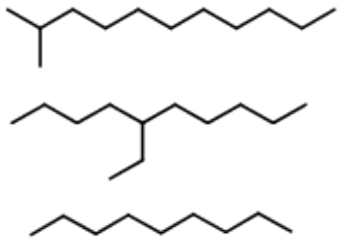
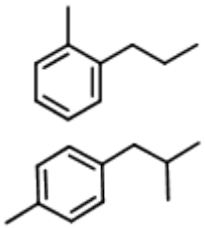
| C-11 |  | + |  C-7 |
| C-10 |  | + |  C-8 |
| C-9 |  | + |  C-9 |
| C-8 |  | + |  C-10 |
| C-7 |  | + |  C-11 |
| C-6 |  | + |  C-12 |
| C-5 |  | + |  C-13 |
| C-4 |  | + |  C-14 |

# Other Products of Hydrothermolysis

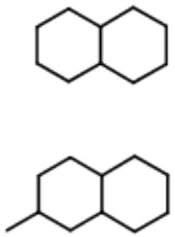
## Isoparaffins



## Alkylbenzenes



## Polycyclics



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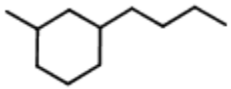
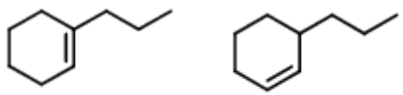
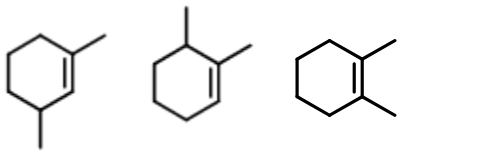
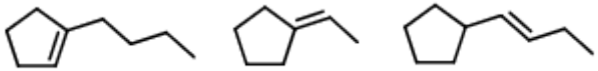


## Olefins







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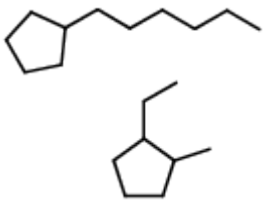
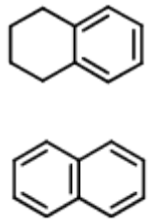
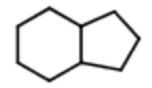
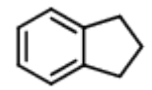








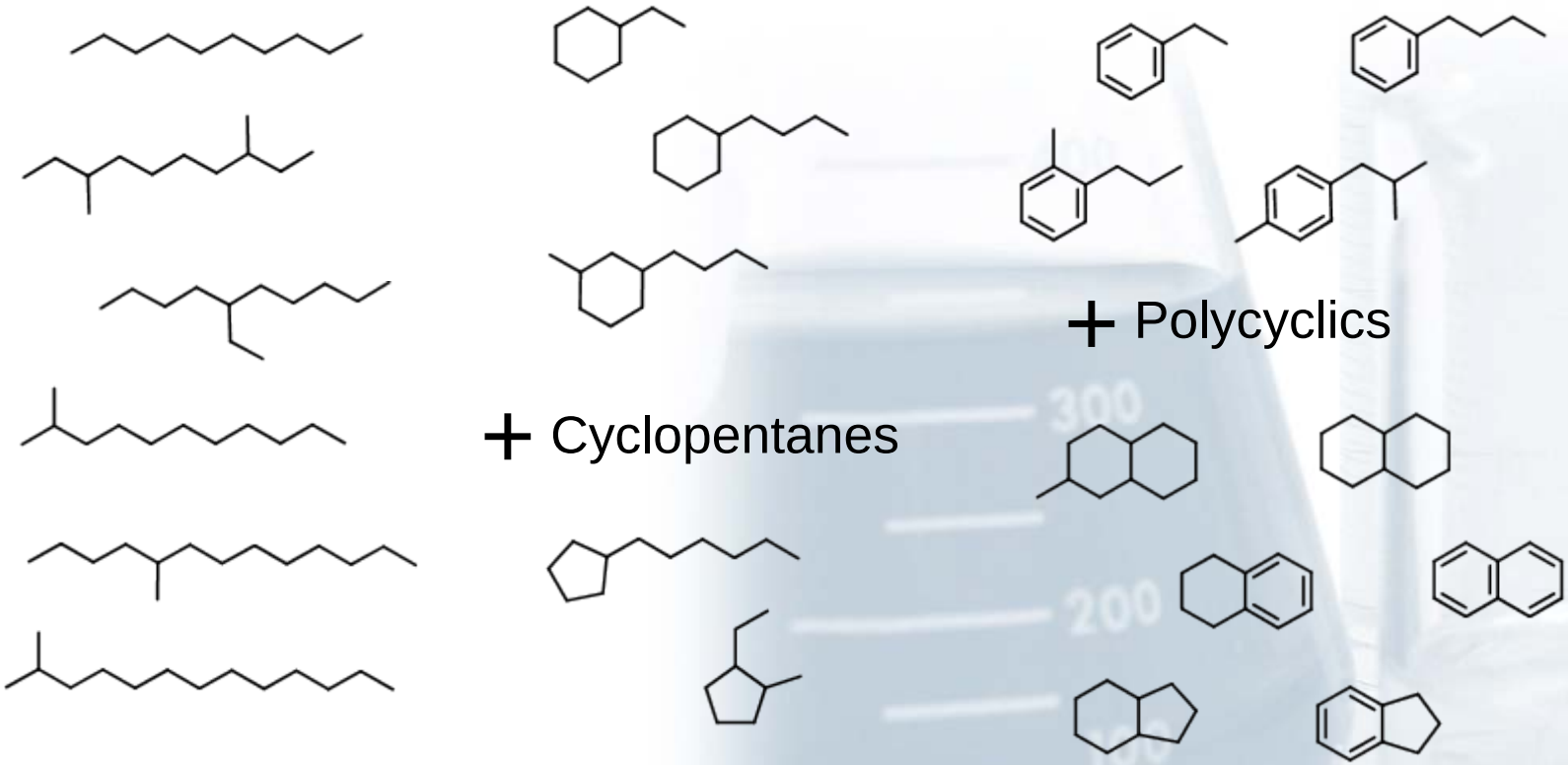


# Typical Alternate Fuel Hydrocarbons

FT & HRJ

Catalytic Hydrothermolysis (CH)

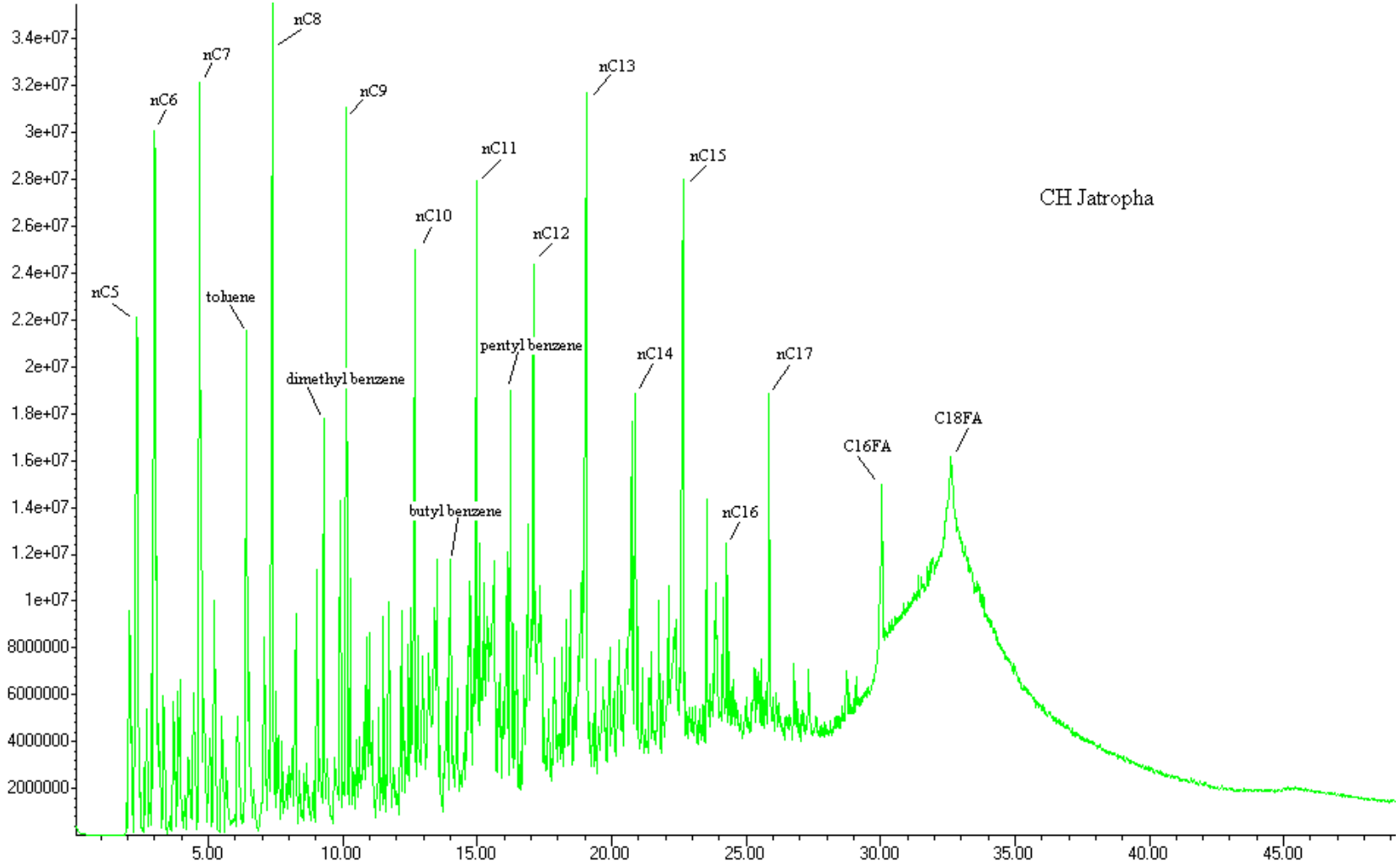
Paraffins + Cyclohexanes + Alkylbenzenes



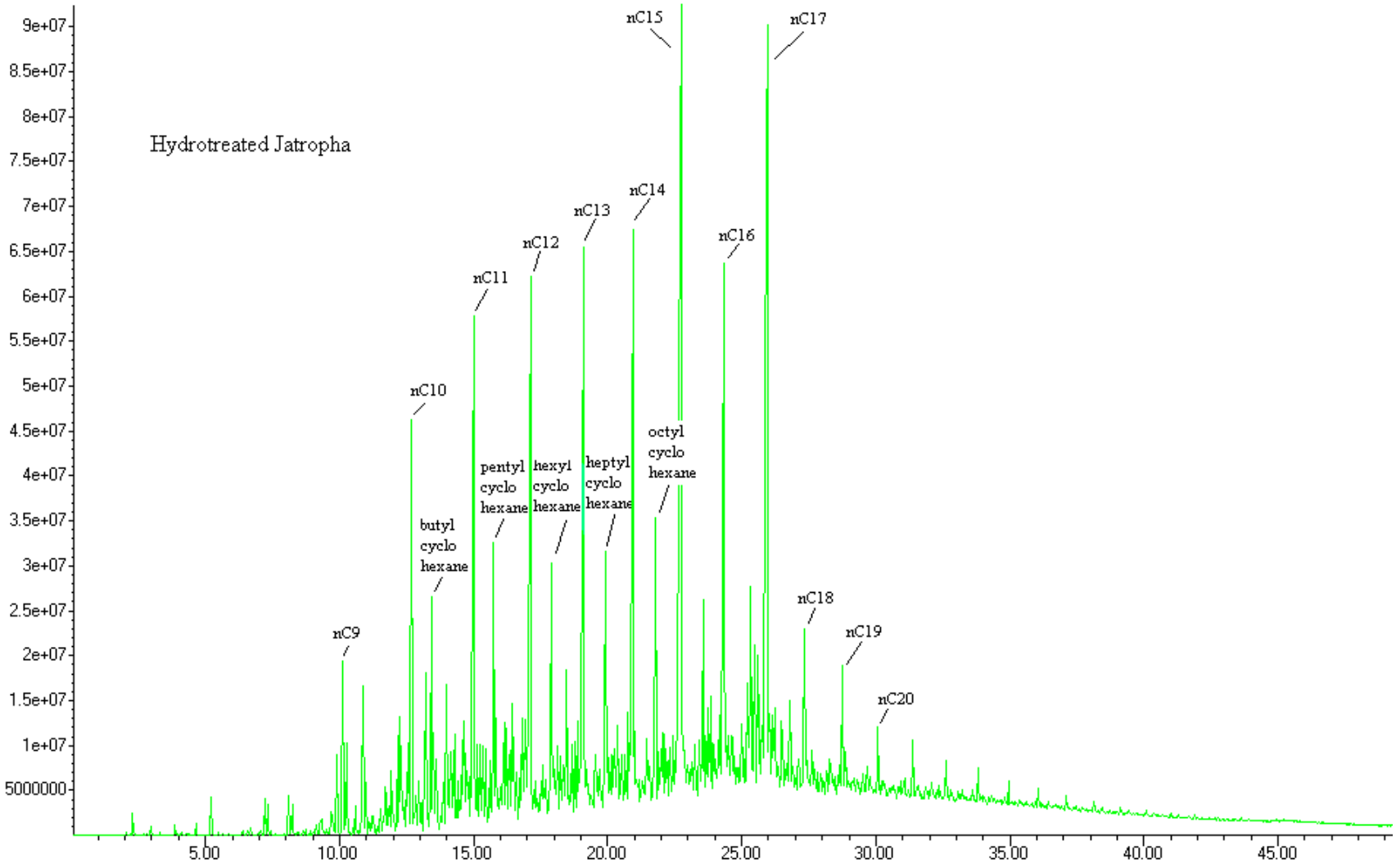
+ Cyclopentanes

+ Polycyclics

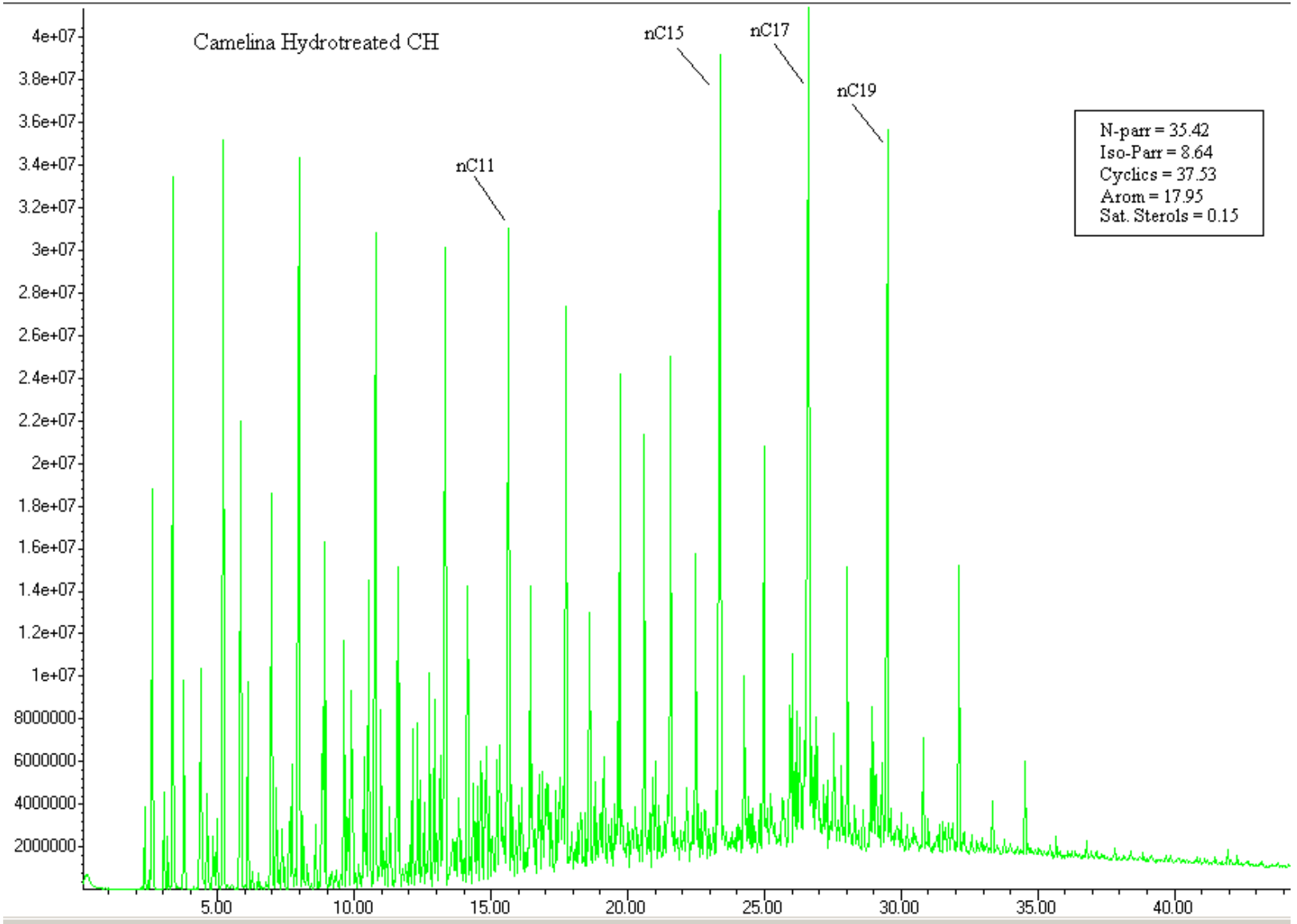
# GC of CH Crude from Jatropha Oil



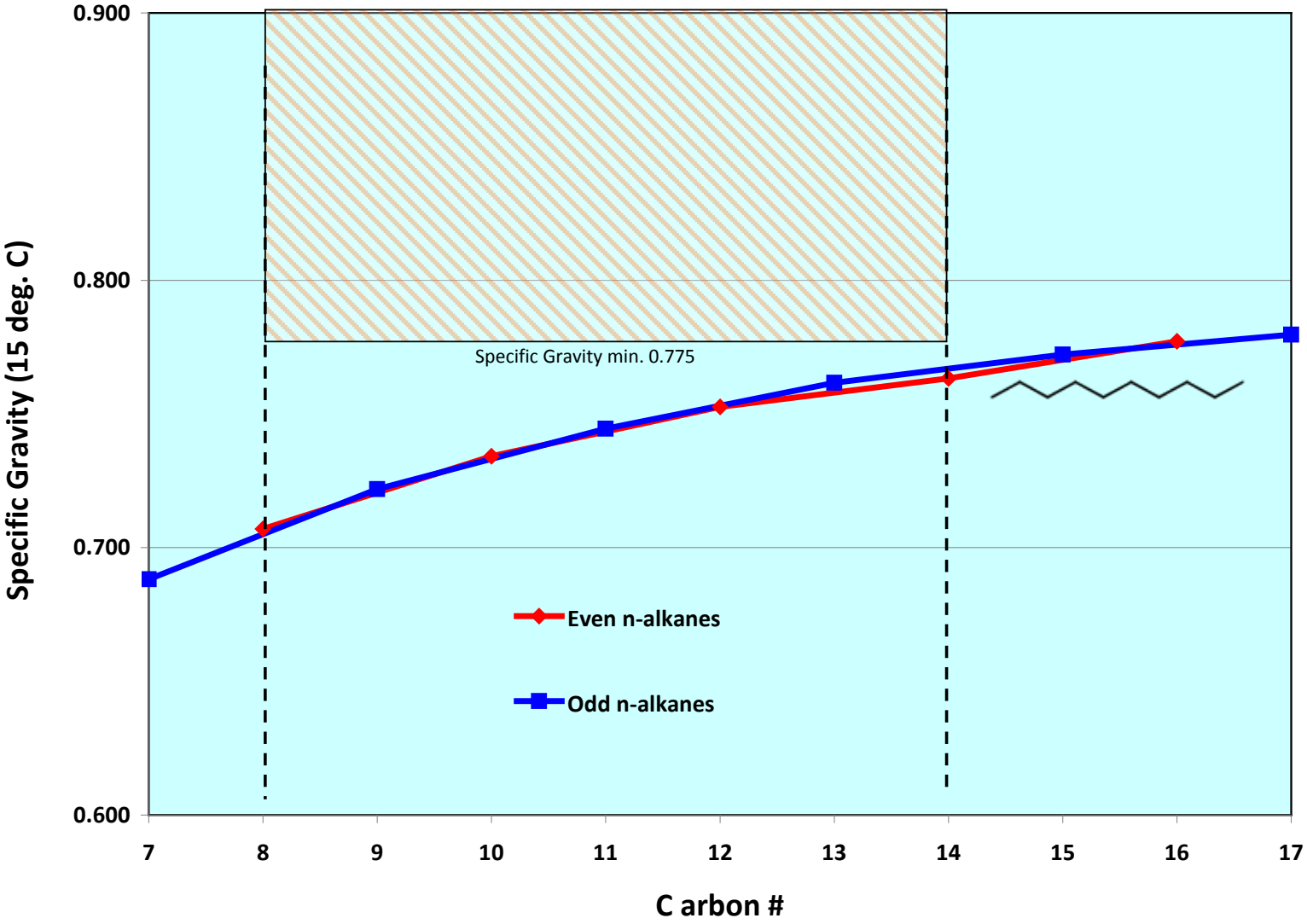
# GC of Hydrotreated CH Crude Jatropha Oil



# GC of Hydrotreated CH Crude Camelina Oil



# Hydrocarbon Type – Specific Gravity Effect



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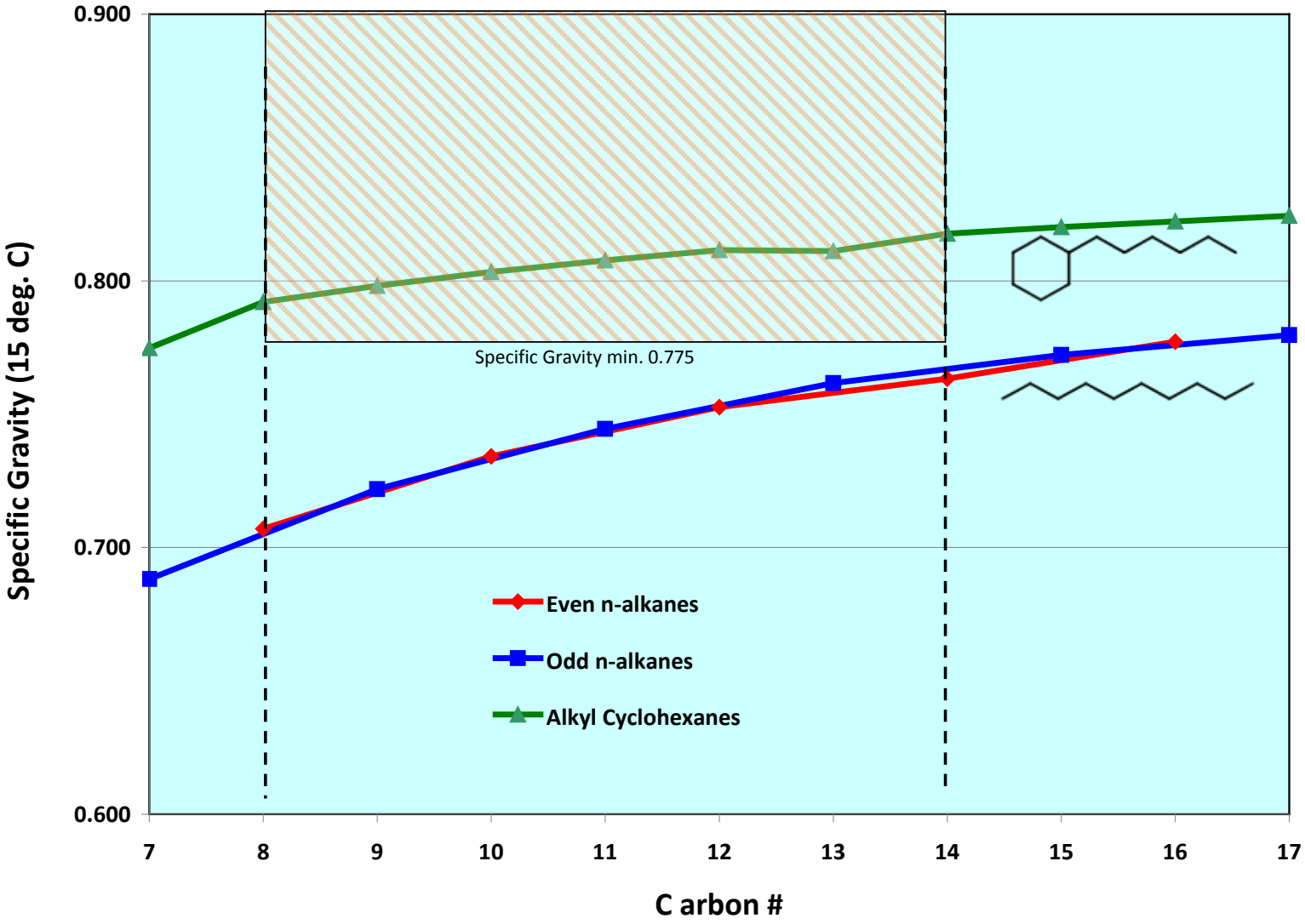

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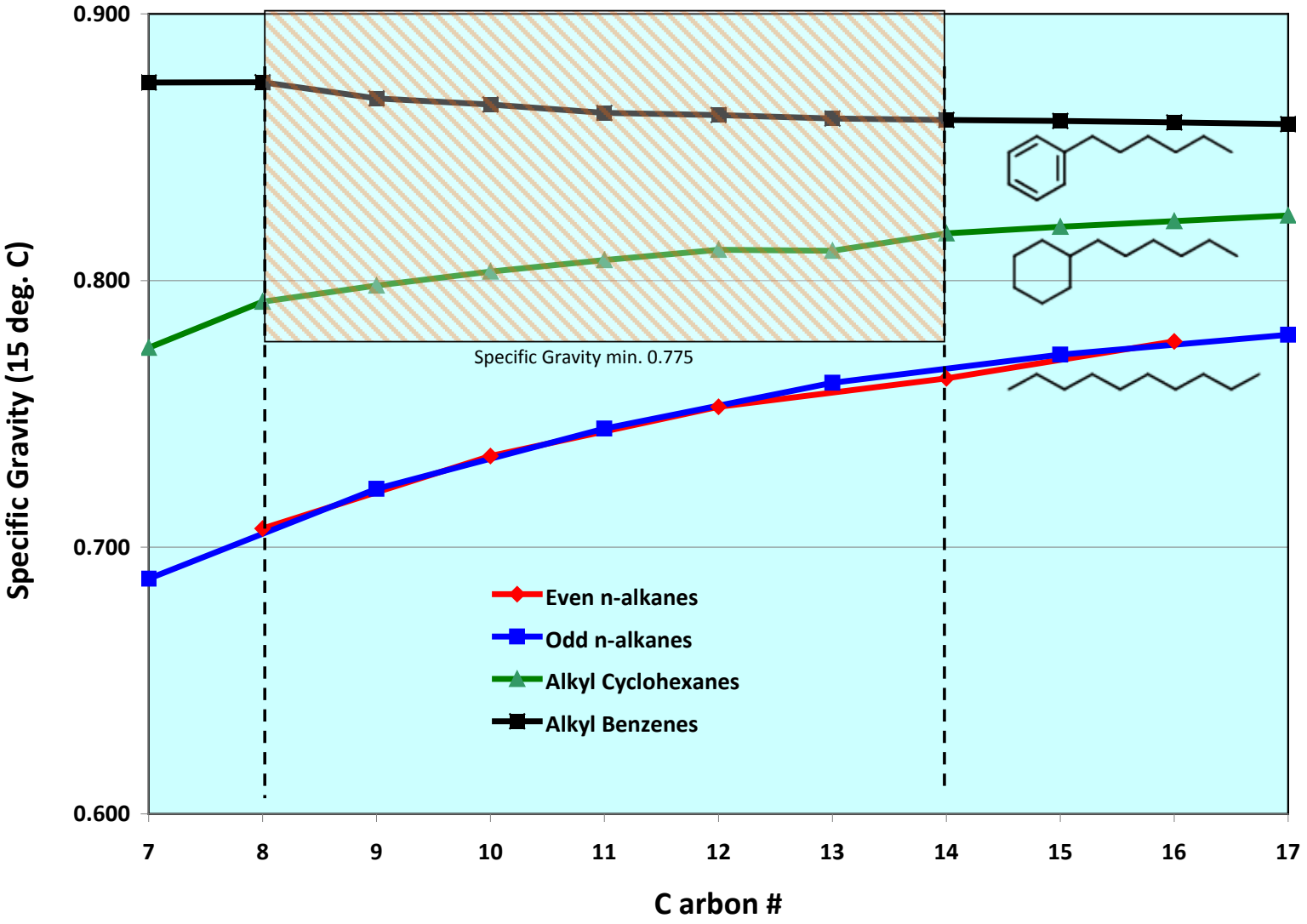
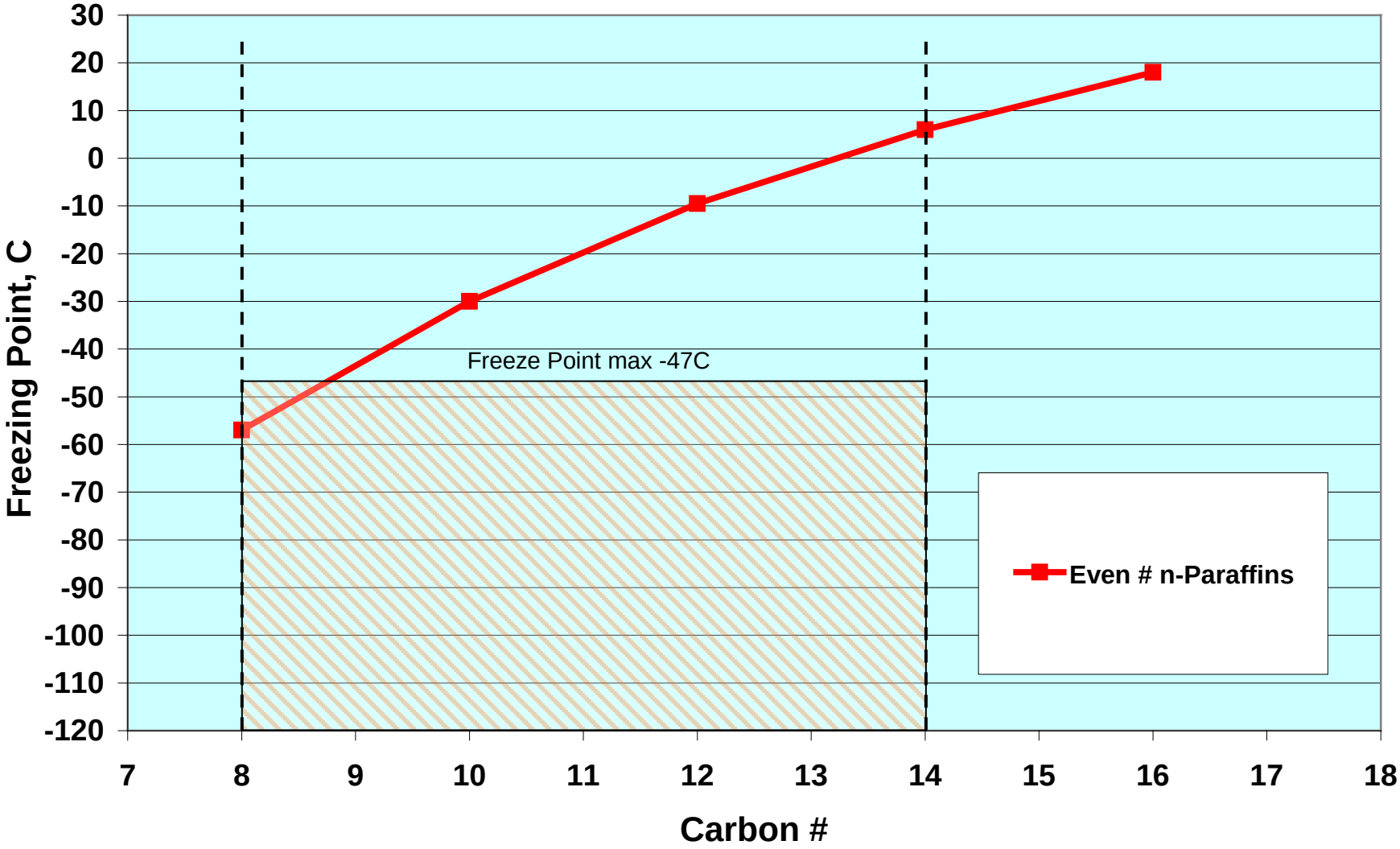
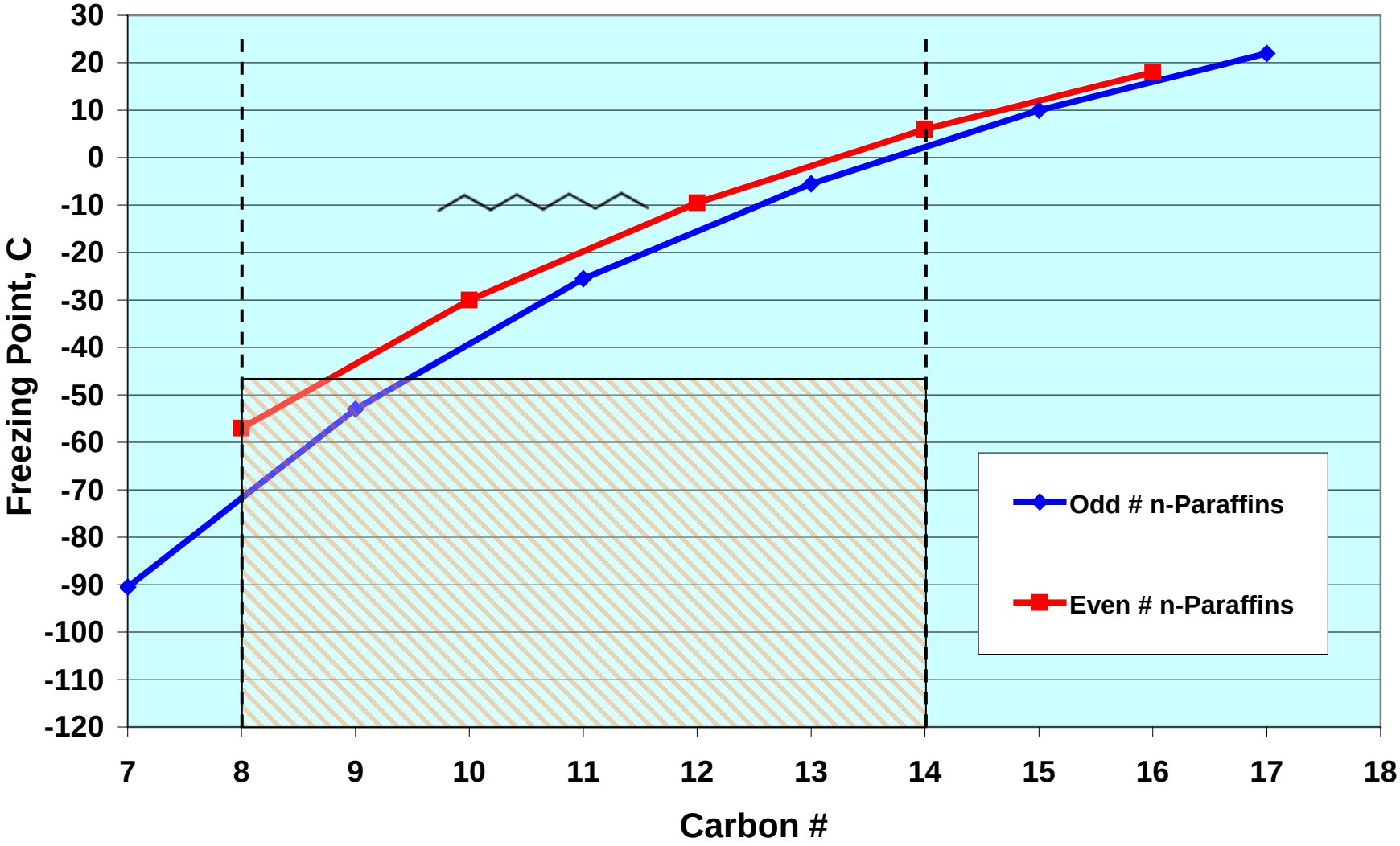


# Hydrocarbon Type – Freezing Point Effect



# Hydrocarbon Type – Freezing Point Effect



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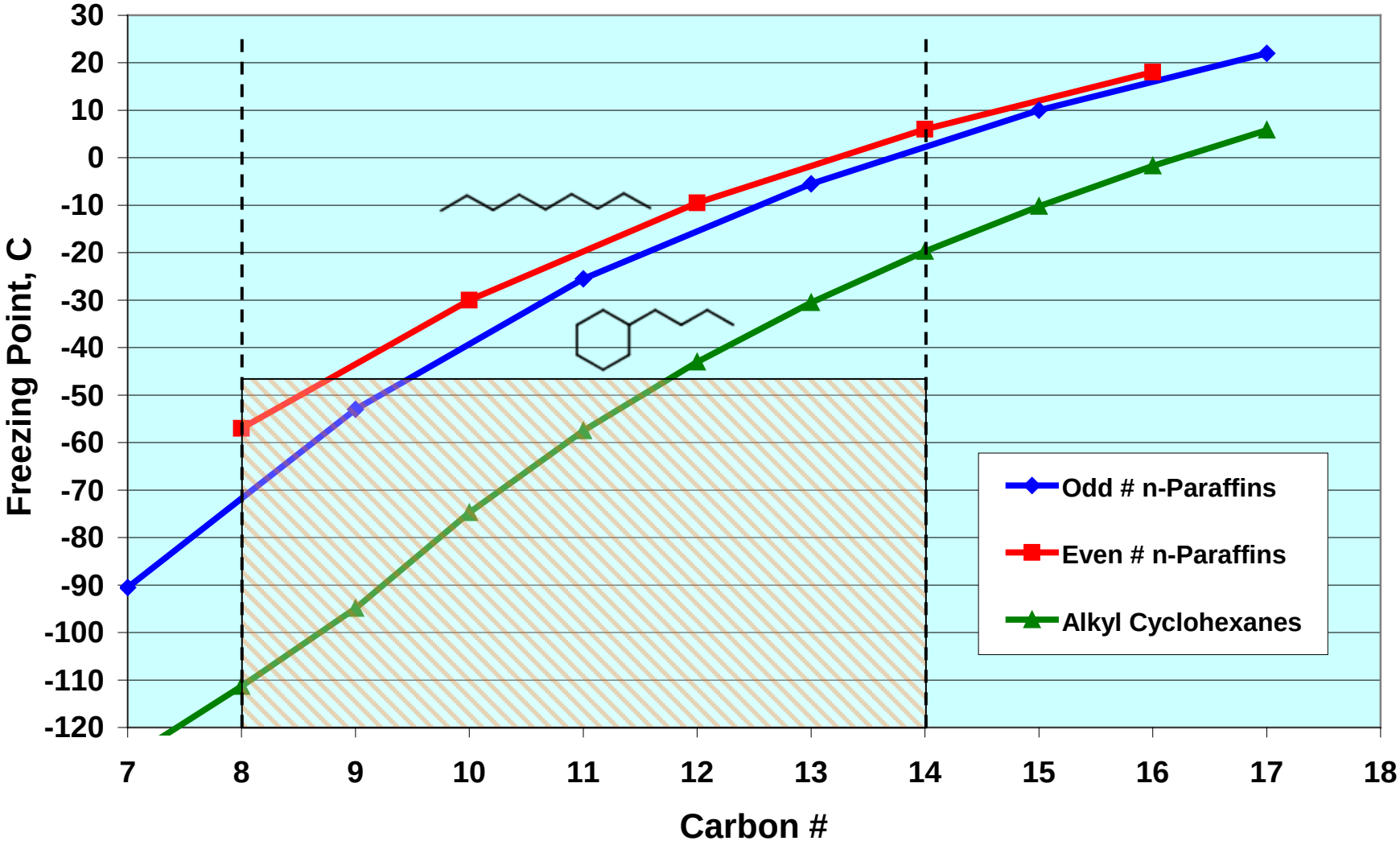

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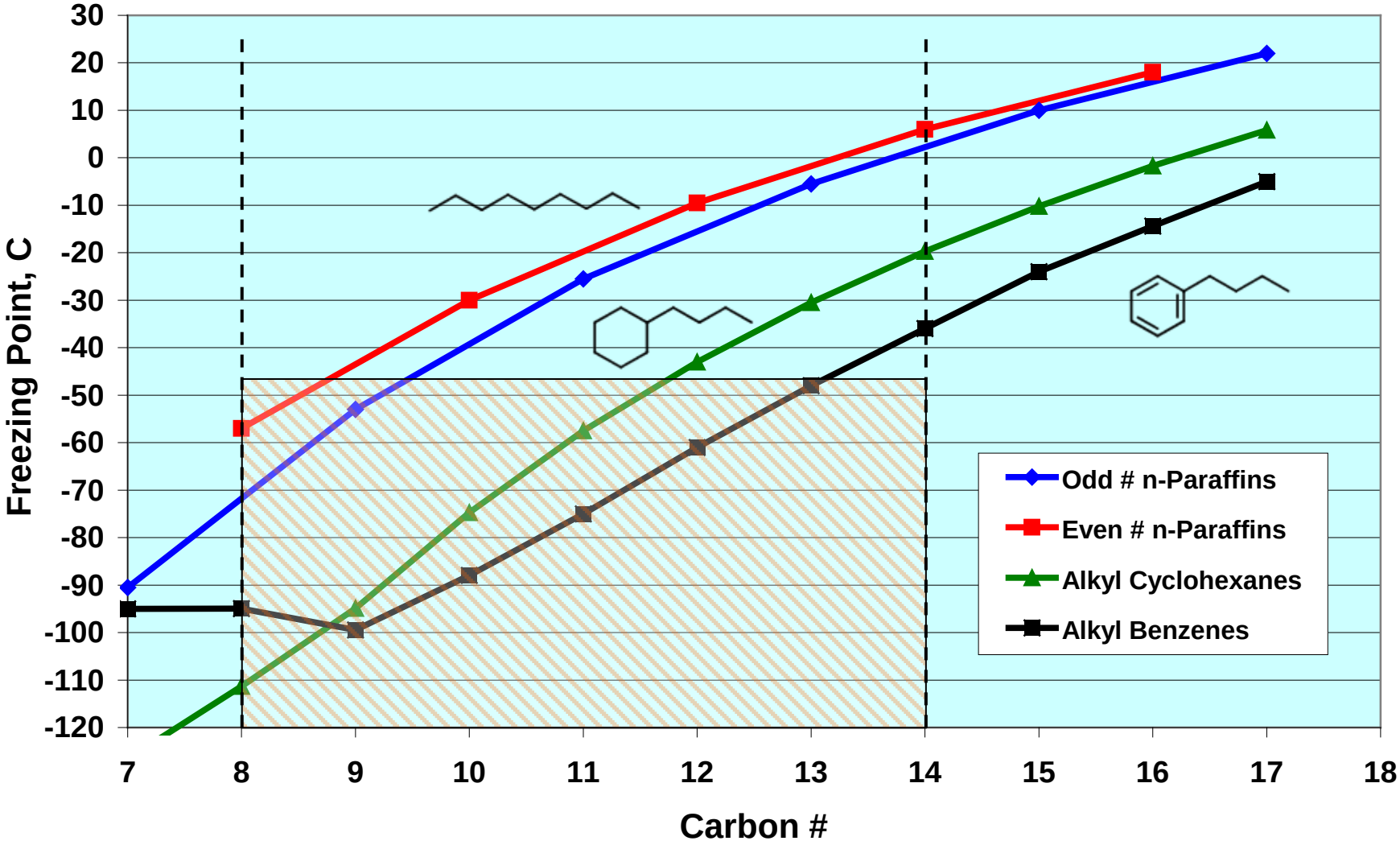
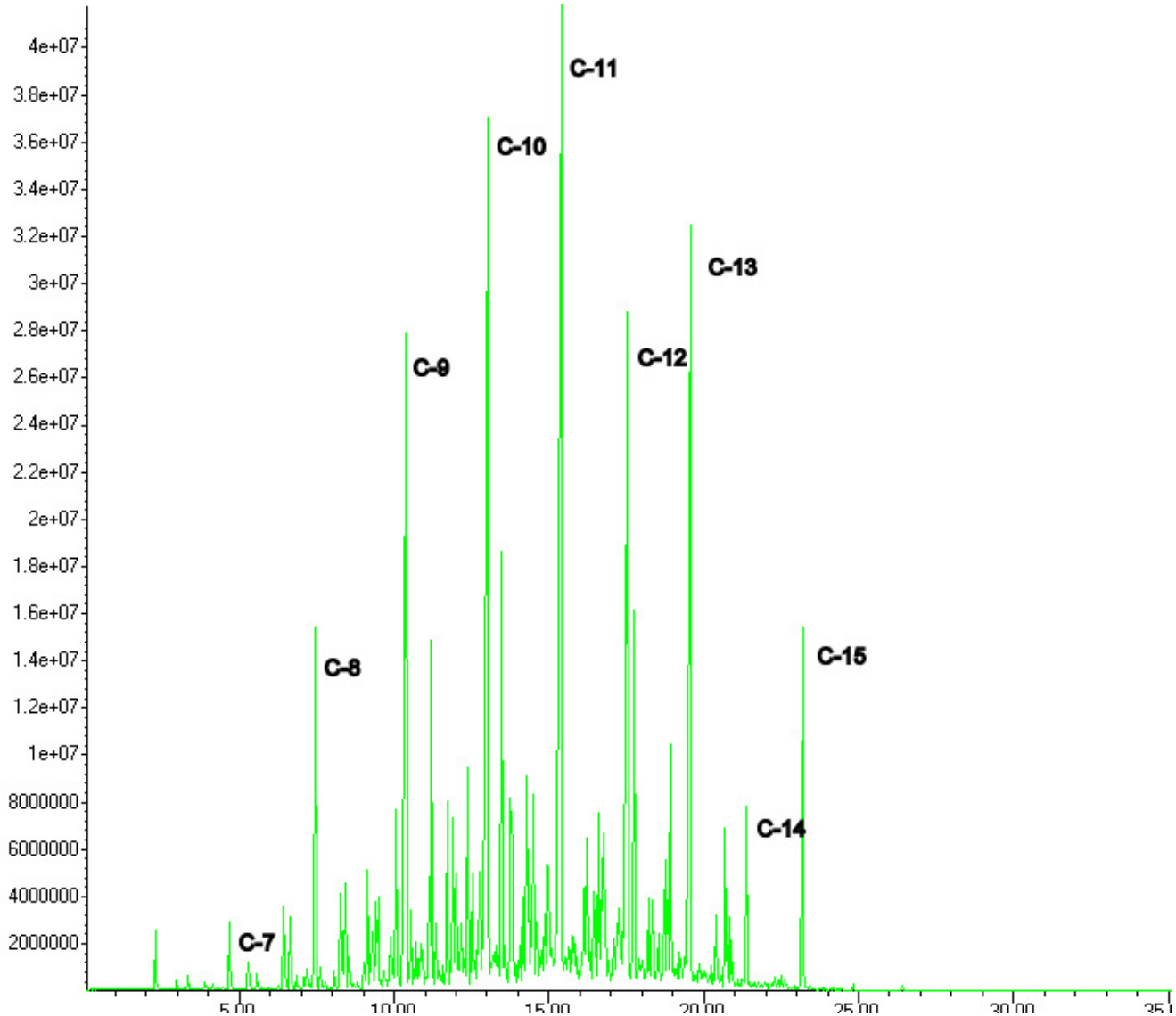


# Properties of ReDi Jet™ and ReDi Diesel™ Fuel Produced by CH

| | ReDi-Jet™ | JP - 8 Spec | ReDi-Diesel™ | F -76** Spec |
|---|---|---|---|---|
| Aromatics, wt% | 11 | 25 max | 14.5 | - |
| Cycloparaffins, vol% | 39 | - | - | - |
| Heat of combustion, MJ/kg | 43.4 | 42.8 min | 43.6 | - |
| Smoke point, mm | 28 | 25 min | - | - |
| Freeze point, °C | <-47 | -47 max | - | - |
| Flash point, °C | 45 | 38 min | 78 | 60 min |
| Density, kg/L | 0.804 | 0.775 min | 0.826 | - |
| Acid #, mg KOH/g | <0.01 | 0.015 max | 0.004 | 0.30 max |
| Hydrogen, wt% | 14.0 | 13.4 min | 14.1 | 12.5 min |
| Cloud point, °C | - | - | -8 | -1 max |
| Pour point, °C | - | - | -9 | -6 max |
| Viscosity @40 °C, cSt | - | - | 3.45 | 1.7-4.3 |
| Demulsification, min | - | - | 1 | <10 |
| Cetane Index | 44 | Report | 62 | >43 |

# GC of Jet Fuel Fraction from Algal Oil

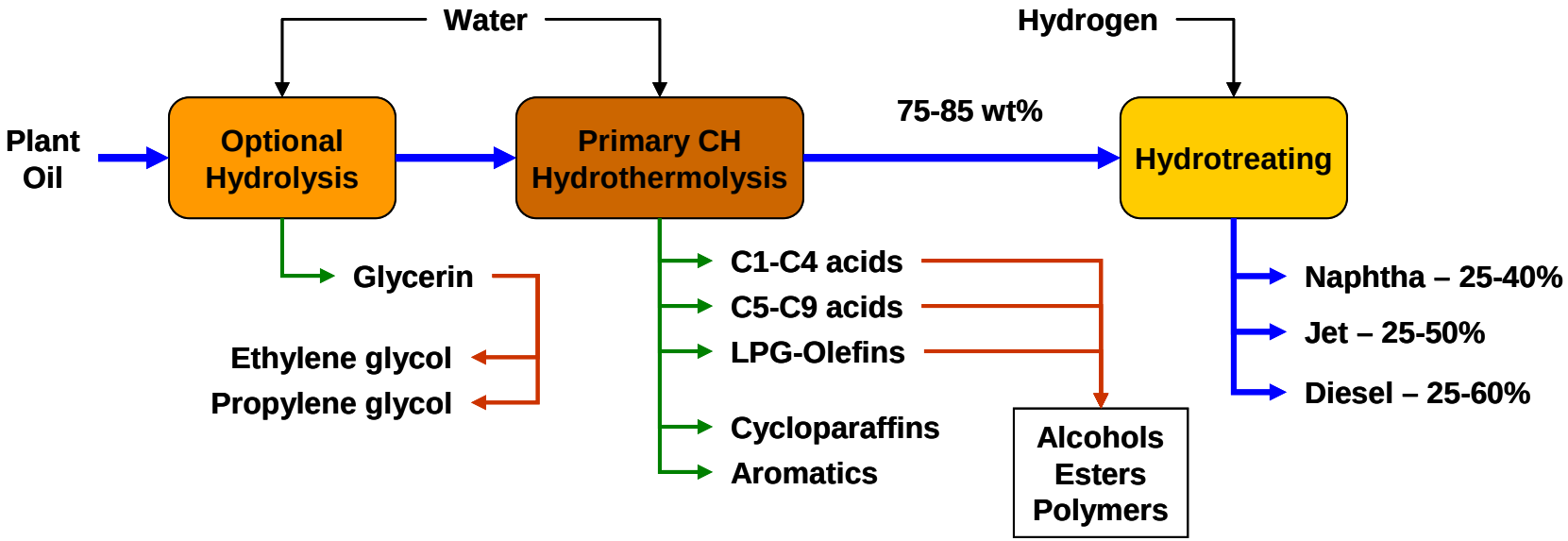


# JP-8 from Algal Oil

- **Refined algal oil from an AFRL contractor**
- **Processed in bench-scale CH unit**
- **Properties are very similar to petroleum reference fuel**
- **Results indicate insufficient hydrotreating for this sample**

| Specification Test | MIL-DTL-83133G | Algal Jet 7451 | Petroleum JP-8 4751 |
|---|---|---|---|
| Aromatics, vol% | < 25 | 18.8 | 18.8 |
| Olefins, vol% | | 1.8 | 0.8 |
| Heat of Combustion, MJ/Kg | >42.8 | 42.7 | 43.3 |
| Flash Point, $^{o}$C | >38 | 40 | 51 |
| Freeze Point, $^{o}$C | <-47 | -49 | -50 |
| Density @15$^{o}$C, Kg/L | 0.775-0.840 | 0.792 | 0.804 |
| **Other Tests** | | | |
| Paraffins (normal + iso), wt% | | 55 | 49 |
| Cycloparaffins, wt% | | 27 | 30 |
| Alkylbenzenes, wt% | | 13 | 13 |
| Indans and Tetralins, wt% | | 4.9 | 5.8 |
| Phenolic Polars by HPLC, mg/L | | 5000 | 160 |

# Product and Byproduct Potential




- Optional two-step CH process for clean glycerin recovery
- Primary and secondary byproducts of higher value
- Less than 5% water consumption
- Up to 100% process water recycle

# Pilot Testing – Panama City, FL

- CH Crude oil production
  - > 24-hour continuous operation
  - Steady-state performance
  - 90-93% FA conversion
  - 5+ gal/hr
- Camelina oil feed
  - Crude and degummed
- CH crude product
  - Water wash
  - Acid no. ~150

# Air Force Research Lab (AFRL)

- Awarded 2nd contract effective 1 Dec 2010
- Primary tasks
  - Optimize 100 gpd pilot system
    - Increase capacity – decrease residence time
    - Conceptual engineering for commercial module
  - Optimize byproduct recovery/value
  - Demonstrate water management
  - Optimization hydrotreating
  - Evaluate additional feed stocks
    - Algal oil, Camelina oil, other plant oils
  - Deliver 150 gallons of CH crude
  - Deliver 100-gal samples of JP-8
    - Different aromatic concentrations
    - Different cycloparaffin concentrations

# Engineering Challenges for Scale up

- CH process
  - Heat transfer - heat recovery
  - Reactor design
    - 3000 psig operating pressure
    - Up to 500°C operating temp
    - Materials of construction
    - Exothermic reaction
    - Turbulent flow
    - Short residence time < 1 min
  - Byproduct optimization
  - Water management
- Hydrotreating
  - Optimize decarboxylation
  - Acid tolerant catalysts
    - Address deactivation
  - Preserve aromatics and cycloparaffins

# Benefits of Catalytic Hydrothermolysis

- Produces high yields of pure hydrocarbon fuels
- Produces cycloparaffin and aromatic compounds
  - Ideal composition for *ReDi* Jet and *ReDi* Diesel fuels
- Produces valuable bio-based chemicals
- Effective for any renewable feed stock
- Reduces hydrogen consumption vs FT & HRJ
- Reduces $CO_2$ emissions vs FT &HRJ
- Minimizes water, chemical, catalyst and energy consumption

fueling the future

# Acknowledgements


- Ed Coppola, Dr Lixiong Li, Jeff Rine, Sanjay Nana, Jonathan Miller, Robert Girvin - ARA
- Robert Allen, Air Force Research Laboratory
- Don Minus, Air Force Research Laboratory
- Ben Curtis, Air Force Petroleum Agency
- Richard Kamin, NAVAIR
- Bill Vasden, USCJO, FFGA